Quantitation and Organic Geochemical Characterization of Petroleum-like Materials Found on An Undisturbed Beach of the Padre Island National Seashore

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A Report Submitted To:

United States Department of the Interior
National Park Service
Southwest Region
P.O. Box 728
Santa Fe, New Mexico 87501

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I. INTRODUCTION

Travers and Luney (1976) listed probable sources of petroleum - like materials found ubiquitous in the oceans of the world. Some of the material (∿15%) is believed to come from natural seepage of oil from incompetent shallow reservoirs. The major part of the oil (∿85%) is apparently anthropogenic in its origin. The major pollution is associated with sea transportation of petroleum and petroleum-derived products.

Tremendous volumes of crude oils are transported daily through the waters of the Gulf of Mexico. In 1979 there were 45.4×10^6 tons of petroleum products which passed through the port of Corpus Christi (Rodman, 1980). This is approximately 750,000 barrels per day. Foreign oil imports into Corpus Christi were about 370,000 barrels per day of which 50 to 60% were from Africa, 20% from the Persian Gulf and about 5% from Mexico. These import and export shipments involve typical tanker operations such as cleaning of cargo holds, releasing sea water ballast and cargo transfers in lightering operations. These types of operations are known to be a major source of introduction of organic residues into the water.

Natural seeps are generally found in petroleum areas where there is pronounced tectonic activity. Such areas are found in southern California, central Mexico, northern South America, the Middle East, etc. The northern Gulf of Mexico is not generally regarded as being of high seepage potential (Wilson, et al., 1973). However, Geyer and Sweet (1973) and Koons and Monaghan (1973) report numerous seeps, primarily gas, in the

Gulf of Mexico with liquid petroleum seeps reported in Mexican waters on the shelf west of the Campeche banks. Geyer and Sweet (1973) attribute to Price (1933) a report of a seep at the northern end of St. Jospeh's Island, however, a review of that work shows that Price was not able to confirm such a seep.

Gas "bubbles" frequently have been observed in "sparker" records of depth and sediment thickness taken along the Continental Shelf off Texas (Watkins and Worzel, 1978). No associated crude oil seeps have been located in those areas. Measurements of stable carbon isotopic composition of methane associated with gas seeps of the Gulf Shelf suggest the gas is largely biogenic ("marsh gas") in its origin, rather than petrogenic ("natural gas") Bernard et al., 1976).

There are, in fact, only few natural oil seeps in the northern Gulf Coast province. On the other hand, numerous seeps are reported in southern Gulf regions from Tuxpan to Tampico. That some of this material finds its way to the shores of the Texas coastal bend region is quite possible and, according to Koons and Monaghan (1973), quite probable.

A large part of crude oil type organic matter added to the marine environment is volatilized or solubilized and thus lost from direct observation (summerized by Wheeler, 1978). That which is not lost may eventually be transported by wind and currents to the beaches where they become an esthetic and economic nuisance. Once on the beaches the oils (tars) may be removed, buried, retransported by ocean water or mixed with

sand and deposited on and in offshore bars and depressions. Except where the materials are physically removed through clean-up campaigns, all of these processes are likely to result in redeposition on the beaches.

There has been little quantitation, other than subjective, of the beach tar material of the Texas Gulf Coast. Coastal residents note a "subjective" increase in beach tar quantity which is roughly correlatable with increased petroleum transportation. That there has been an influx of tar on Texas beaches has been well known for a long time. Karankawa Indians used asphalts in pottery of pre-Columbian age found on Padre Island (see Geyer and Sweet, 1973).

On June 3, 1979 the IXTOC I well in the Bay of Campeche "blew out" with the subsequent release of 3 to 4 million barrels of oil. A major portion of that oil is known to have escaped recovery or was deliberately dispersed into the environment. This catastrophic source appears to be a major contributor to coastal water petroleum residues of the Gulf.

Two questions which arise are: 1) What quantities of this petroleum-like material are being deposited annually on the south Texas beaches? And 2), is there a single source of beach tar (seeps) or are there multiple sources (spilled or dumped crudes as well as seeps)? This study is part of an effort to find answers to these questions.

II. EXPERIMENTS AND RESULTS

A. Quantitation of Beach Tar

Two sites for study were selected at the southern end of North Padre Island in an area of the Padre Island National Seashore which is not generally accessible by two-wheel-drive vehicles. Transects #1 and #2 were located 1.6 and 3.5 kilometers south of the "barricade" for two-wheel-drive vehicles. Each site was a two meter wide strip of the beach from the low tide line to the base of the dunes marked off by stakes set in the sand.

All pre-existing tar-like material was cleaned as much as possible from the staked areas. The sites were reoccupied after a three day accumulation period and all tar-like material was collected for analysis. When possible, the samples were taken at a time of low tide. Sampling was on alternate months starting in December of 1978.

For the December 1978 collection of transect #1 a single, large tarball was found within the transect area which was unlike other material collected within the transects (or observed outside the transects). This tarball was collected as a separate sample. For the sampling of February, 1979 at both transects, material was collected from three distinct strand lines labeled "high", "middle", and "low". A total of fifteen samples were collected from two transect sites on five collection dates from December of 1978 to August 1979. The quantities of petroleum-like organic materials recovered from the samples are listed in Table I. These quantities represent the total

extractable beach tar recovered from the sites, the quantity extrapolated to equivalent material per kilometer of beach per day, and the quantity expressed as metric tons per year for each kilometer of beach front.

The February, 1979 sampling followed a relatively large oil spill of unknown origin. This spill was cleaned from the beach under the direction of the U.S. Coast Guard and National Park Service personnel. While most of the materials accummulating in the study areas was removed, some residues of the spill were noted, especially in the material recovered from the high strand line.

The collection in August, 1979 followed the beginning of the influx of "Mousse" to south Texas shores resulting from the IXTOC I blow-out in the Bay of Campeche. The transect sites were cleaned on August 13, 1979, with very little tar being reported. On August 14, 1979 the first report of IXTOC I Mousse on Mustang Island (25 kilometers North of the collection sites) was confirmed. On the collection date of 16 August, 1979, the field notes report "..a fairly large amount of oil, apparently Mexican, on the beach and there was also a lot (of oil) in the water actively washing up.." Within a few days of the collection the entire coastal beaches of south Texas from mid-San Jose' (St. Joseph's) Island to Port Isabel had received the full impact of the IXTOC I accident. The study was concluded following the influx of IXTOC I oil.

B. Chemical Characterization

Collected beach tars were chemically characterized by methods typical of the petroleum industry characterization of crude petroleums. That is, asphaltenes were precipitated and the residues were separated into fractions containing predominantly alkanes, aromatics, and compounds including the "hetero-elements"-nitrogen, sulfur, and oxygen (NSO's). Glass-capillary gas chromatography was used in analysis of the alkane fraction and all fractions were characterized by measurement of stable carbon isotopic compositions.

1. Methods

a. Extraction

Material collected from the beach generally contained sand and debris other than the petroleum-like organic material. The sample, or a known portion of it, was placed in a large (250 milliliter capacity) Soxhlet extractor and was continuously extracted with benzenefor approximately twenty-four hours. For these loose, sandy tar samples, this extraction procedure effectively recovered all tar, even from water wet samples.

b. Asphaltenes Precipitation

Benzenewas removed from the extract by a stream of air filtered through a silica gel bed to remove extraneous hydrocarbons. The air dried extract was weighed and taken up in a minimal amount of benzene. An excess (about 20-30 volumes) of pentane was added to the benzene solution and the mixture was chilled to 5 °C to precipitate the asphaltene fraction. The

asphaltenes were filtered and weighed and preserved for isotopic analysis.

c. Silica-Gel Chromatography

The pentane soluble material from the asphaltenes precipitation step was added to the top of a 1 cm by 20 cm column of silica-gel (Woelm, Activity I). The column was successively eluted with three column volumes (50 ml) each of hexane, benzene: hexane (1:1), and methanol. These three fractions recovered contained saturate hydrocarbons, aromatic hydrocarbons, and polar organic compounds (NSO's) respectively.

d. Stable Isotopic Determination

Five fractions of each sample (total extract, asphaltenes, saturate, aromatic, and NSO compounds) were analysed for stable carbon isotopic composition. Each fraction was combusted in a vacuum combustion system modified from Craig (1953) to give carbon dioxide suitable for introduction into an isotope ratio mass spectrometer. Either a Nuclide Model RMS-6 or a V-G Micromass Model 602-E mass spectrometer was used for isotopic measurement. Both instruments are equipped with dual inlets and dual detectors (McKinney, et al., 1950) to allow precise comparison of the unknown sample with an arbitrary standard sample. Results are reported, according to standard practice, in "del-value" units, which are the parts per thousand difference in the $^{13}C/^{12}C$ ratios for the unknown sample and an arbitrary standard. In this work the arbitrary standard for reporting is the PDB carbonate standard.

e. Gas Chromatographic Analysis

Each of the fifteen saturate fractions was analyzed by glass capillary gas chromatography. The instruement used was a Perkin-Elmer Model 910 with a twenty-seven meter glass capillary column coated with OV-101 stationary phase. A Hewlett-Packard Model 3352B data system was used for digital integration of the chromatographic peaks. Relative amounts of the individual n-alkanes from n-C14 through n-C38 were obtained. Relative amounts of the isoprenoid hydrocarbons pristane and phytane were also measured.

Results of chemical and physical measurements are presented in Tables II and III with some of the ratio-type parameters reported in Table IV. The normalized values of n-alkanes for each samples are reported in Fig. 1, while OEP-plots (Scalan and Smith, 1970) calculated from these n-alkanes distributions are given in a Fig. 2.

III. DISCUSSION AND CONCLUSIONS

Quantitation

With respect to the answer to the first of the two primary questions of the introduction, "what quantities of... petroleum-like material are being deposited annually on the south Texas beach?" The conclusion is that this objective of the study was not met. The primary reason is that the experimental design failed to account for lateral movement of tar-like materials from areas adjacent to the collection site

into the sampling area. The material deposited may, in some cases, represent as much old material redistributed on the beach as it does new material freshly deposited.

Where the entire beach had been freshly cleaned, as in the February collection, the amounts may be a realistic estimate of material newly accumulated on the beach. All quantities may better represent a measure of the "standing crop" of material on the beach. In one case (June, 1979) the field notes report "...not much lateral movement into (the) transects..."

The values of Table I Column 2 would have to be multiplied by 3 (3 days accumulation) in order to estimate the standing tar load. The result gives the equivalent of approximately 0.32 metric tons per kilometer for a high (April, 1979 - Transect #2) and a low of approximately 5.5×10^{-5} metric tons per kilometer (February 1979 - Transect #1 Middle). The average annual accumulation is 11.3 metric tons per kilometer of beach front. A similar study of tar on the beaches of San Jose' Island gave a fortuitously coincident value of 10.2 metric tons per kilometer per year (Scalan and Winters, 1980).

Sources

The second question asked in the introduction "is there a single source of beach ... or are there multiple sources...? is a little more easily approached. Ratios of components and isotopic compositions suggest multiple sources for the materials found on the beaches of the Padre Island National Seashore. Some measured parameters are known to be highly dependent upon

the amount of "weathering" the petroleum-like matter has undergone, others may be insensitive to weathering.

The amount of asphaltenes present in a sample is partially related to the amount of oxidative weathering a sample has undergone. Thus samples with less than ten percent asphaltenes are not believed to have been oxidized to any great extent. Some samples of petroleum may be naturally high in asphaltene content because they are not "mature" oils or because they have been in contact with oxygenated waters in the reservoirs. Samples from December, Transect #2; February, Transect #1, Middle; and February Transect #2 - high are most likely not highly weathered.

Relative distributions of n-alkanes present a convenient means of comparing samples for similarities. While weathering and biological degredation may alter these distributions, their effects are not likely to create the wide variety of distributions seen in Figure 1. Bimodal and even trimodal distributions are seen. This probably indicates a certain amount of mixing of hydrocarbon from various sources. No attempt was made to separate different "types" of tar particles at the time of collection.

A parameter that is relatively insensitive to weathering and derived from n-alkanes distribution is the OEP curve or distribution of odd-even-predominance (Scalan and Smith, 1970). This is a measure of the ratio of n-alkanes having an odd number of carbon atoms to those having an even number. It can be used as a kind of "fingerprint" for correlation of

crude oils. The OEP curves in Figure 2 also suggest a wide variety of sources for the tar samples collected.

Recommendations

This study failed to account for long-shore transport of beach tars from adjacent areas into the sampling transect. This might be remedied by:

1. Cleaning the tar from areas adjacent to the sampling site to prevent its redistribution; and

2. Making the sampling site considerably larger and measuring the distribution of tar within the sampling site. These measures would entail a much larger effort either in the field or in the laboratory or both.

The conclusions are drawn from a relatively small number of samples. Both the number of sampling locations and the frequency of sampling should be increased to give a realistic evaluation of annual and spatial variations. This would also involve a much larger effort in the field and the laboratory.

Due to lack of manpower, time, and funds the geochemical characterizations of this study were minimal. A more detailed study of the various fractions separated from the tar by such techniques as gas/chromatography- mass spectrometry, high-performance-liquid-chromatography, fluorescence spectrophotometry nuclear-magnetic-resonance, etc., would be useful in establishing the nature of the samples.

Acknowledgements

The study was made possible through the combined efforts of Scott Holt and Nancy Rabalais in the field and Dan Boatwright

and Della Scalan in the laboratory. The assistance of Jim Woods and the personnel of the National Park Service is appreciated.

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Table I.

Quantities of Beach Tar Collected From Two Transects From Padre Island National Seashore

Sample		Total Accumulated Tar		
		Grams*Day^{-1}	Grams*Kilometer^{-1}*Days^{-1}	Metric Tons * Kilometers^{-1} * Years^{-1}
December 23, 1978 -				
Transect #1		0.151		
Transect #2		0.874	3,774	1.4
Lone Tar Ball		14.07		
February 22, 1979 -				
Transect #1	Low	0.246		
	Middle	0.037		
	High	4.068	5,787	2.1
Transect #2	Low	0.280		
	Middle	3.717		
	High	14.80		
April 21, 1979 -				
Transect #1		184.7		
Transect #2		216.0	100,175	36.5
June 21, 1979 -				
Transect #1		44.0		
Transect #2		60.0	26,000	9.5
August 16, 1979 -				
Transect #1		36.3		
Transect #2		39.5	18,950	6.9

Table II

Separated fraction of beach tar samples from Padre Island National Seashore study

Sample		Relative weight percentages			
		Asphaltenes	Saturates	Aromatics	NSO's
December 23, 1978					
Transect #1		15.0	49.5	14.3	21.1
Transect #2		6.5	48.4	22.0	23.1
Lone tar ball		24.8	8.3	27.1	39.8
February 22, 1979					
Transect 1	Low	17.0	49.8	10.9	22.3
	Middle	6.8	54.6	21.8	16.8
	High	13.0	55.4	19.8	11.8
Transect #2	Low	13.3	46.7	27.3	12.7
	Middle	20.5	38.2	32.2	9.1
	High	7.1	52.5	30.0	10.4
April 21, 1979					
Transect #1		28.4	45.1	15.1	11.4
Transect #2		30.7	45.7	14.7	8.8
June 21, 1979					
Transect #1		21.2	51.1	18.3	9.5
Transect #2		22.2	51.6	16.4	9.8
August 16, 1979					
Transect #1		32.1	35.8	13.8	18.4
Transect #2		20.1	37.9	16.6	25.4
Malaqite Beach Spill February 16, 1979		7.6	51.2	36.8	6.0

Table III

Stable carbon isotopic composition of fractions of beach tars from Padre Island National Seashore

Sample		$\delta^{13}C$ PDB				
		Whole Tar	Asphaltenes	Saturates	Aromatics	NSO's
23 December, 1978						
Transect #1		-26.8	-27.1	-27.1	-26.4	-26.4
Transect #2		-27.1	-26.8	-27.2	-26.1	-26.0
Lone Tarball		-27.4	-28.4	-27.4	-27.6	-27.7
22 February, 1979						
Transect #1	Low	-27.9	-27.9	-27.6	-26.8	-26.8
	Middle	-27.4	-27.1	-27.2	-26.1	-26.2
	High	-28.1	-27.3	-27.6	-27.6	-26.3
Transect #2	Low	-27.5	-27.2	-27.4	-27.3	-26.4
	Middle	-27.0	-27.3	-28.1	-26.9	-26.6
	High	-27.0	-26.9	-26.9	-26.2	-26.4
21 April, 1979						
Transect #1		-28.2	-28.1	-27.2	-27.1	-26.4
Transect #2		-27.7	-28.0	-27.8	-27.1	-26.2
21 June, 1979						
Transect #1		-26.9	-28.0	-27.2	-26.4	-26.1
Transect #2		-27.3	-27.6	-27.0	-26.7	-28.7
16 August, 1979						
Transect #1		-27.1	-27.7	-27.3	-27.3	-27.1
Transect #2		-27.1	-27.1	-27.3	-26.5	-27.4
Malaquite Beach Spill		-27.2	-26.6	-28.0	-26.6	-26.0

Table IV

Some ratio-type geochemical parameters of beach tar samples from the Padre Island National Seashore.

Sample		Pristane/ Phytane	Pristane/ $n\text{-}C_{17}$	Phytane/ $n\text{-}C_{18}$	$n\text{-}C_{17}$/ $n\text{-}C_{18}$
December 23, 1978					
Transect #1 *		-			
Transect #2 **		.95	-	-	-
Lone Tarball *					
February 22, 1979					
Transect #1	Low	1.16	6.64	5.92	1.04
	Middle	1.19	1.81	1.40	0.92
	High	1.11	0.82	0.66	0.89
Transect #2	Low	1.02	1.85	1.38	0.76
	Middle	0.60	0.25	0.50	1.19
	High	1.47	1.10	0.68	0.90
April 21, 1979					
Transect #1		1.39	0.72	0.52	1.01
Transect #2		1.25	0.87	0.65	0.94
June 21, 1979					
Transect #1		1.78	0.92	0.49	0.95
Transect #2		1.64	0.75	0.41	0.90
August 16, 1979					
Transect #1		0.44	0.53	0.64	0.54
Transect #2		0.49	0.50	0.61	0.60
Malaquite Beach Oil Spill		1.15	0.60	0.43	0.83

* These samples contained no isoprenoid or n-alkane saturates of carbon number less than C_{21}.

** This sample contained isoprenoids but no n-alkanes of carbon number less than C_{21}.

Figure 1. Distribution of n-alkanes in samples of beach tar from Padre Island National Seashore.

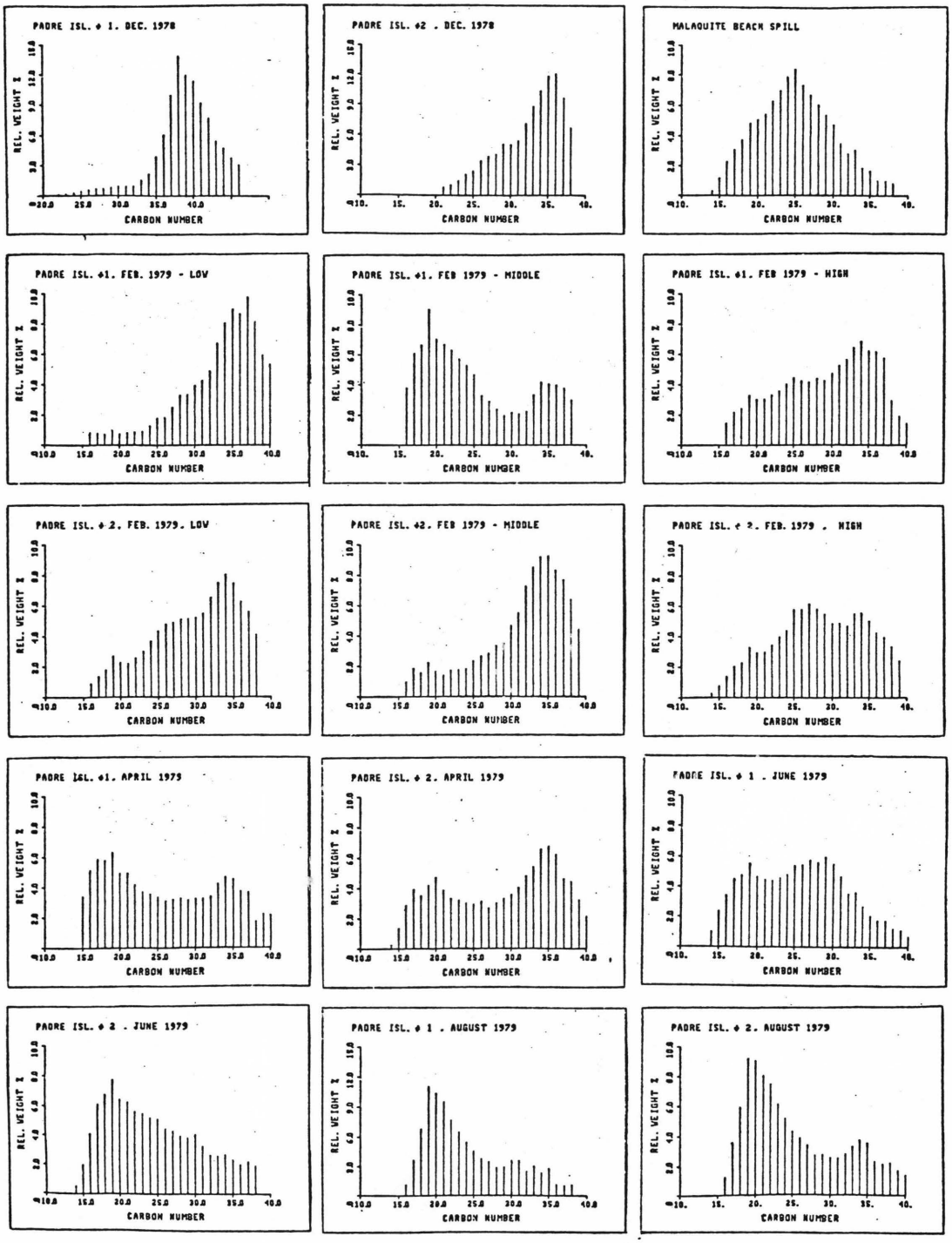

Figure 2. OEP curves for samples of beach tar from Padre Island National Seashore.